



US009410098B2

(12) **United States Patent**
D'Amore et al.(10) **Patent No.:** **US 9,410,098 B2**
(45) **Date of Patent:** **Aug. 9, 2016**(54) **PROCESS FOR MAKING ISOOCETENES
FROM AQUEOUS ISOBUTANOL**

- (71) Applicant: **Butamax Advanced Biofuels LLC**,
Wilmington, DE (US)
- (72) Inventors: **Michael B D'Amore**, Wilmington, DE
(US); **Leo Ernest Manzer**, Wilmington,
DE (US); **Edward S Miller, Jr.**,
Knoxville, TN (US); **Jeffrey P Knapp**,
Wilmington, DE (US)
- (73) Assignee: **Bitamax Advanced Biofuels LLC**,
Wilmington, DE (US)
- (*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 62 days.

(21) Appl. No.: **13/967,696**(22) Filed: **Aug. 15, 2013**(65) **Prior Publication Data**

US 2014/0005443 A1 Jan. 2, 2014

Related U.S. Application Data

- (63) Continuation of application No. 11/818,354, filed on
Jun. 13, 2007, now abandoned.
- (60) Provisional application No. 60/814,153, filed on Jun.
16, 2006.

(51) **Int. Cl.**

C07C 1/22 (2006.01)
C07C 29/04 (2006.01)
C07C 41/06 (2006.01)
C10L 1/16 (2006.01)
C07C 1/20 (2006.01)
C07C 5/03 (2006.01)
C07C 9/21 (2006.01)
C10L 1/18 (2006.01)
C12P 5/02 (2006.01)
C10L 1/182 (2006.01)
C10L 1/185 (2006.01)

(52) **U.S. Cl.**

CPC ... **C10L 1/16** (2013.01); **C07C 1/20** (2013.01);
C07C 1/22 (2013.01); **C07C 5/03** (2013.01);
C07C 9/21 (2013.01); **C07C 29/04** (2013.01);
C07C 41/06 (2013.01); **C10L 1/18** (2013.01);
C12P 5/026 (2013.01); **C07C 2521/08**
(2013.01); **C07C 2527/054** (2013.01); **C07C**
2529/18 (2013.01); **C07C 2529/40** (2013.01);
C07C 2531/10 (2013.01); **C10G 2300/4006**
(2013.01); **C10G 2300/4012** (2013.01); **C10G**
2300/805 (2013.01); **C10G 2400/22** (2013.01);
C10L 1/1608 (2013.01); **C10L 1/1824**
(2013.01); **C10L 1/1852** (2013.01); **C10L**
2200/0469 (2013.01); **C10L 2270/023**
(2013.01); **C10L 2270/026** (2013.01); **C10L**
2270/04 (2013.01); **C10L 2290/26** (2013.01)

(58) **Field of Classification Search**

None

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

2,228,662 A * 1/1941 Holm C10L 1/023
44/356

4,374,859 A 2/1983 Kunkee et al.
4,450,294 A 5/1984 Feldman
4,628,116 A 12/1986 Cenedella
5,288,924 A 2/1994 Beech, Jr. et al.
5,755,967 A 5/1998 Meagher et al.
6,358,717 B1 3/2002 Blaschek et al.
7,993,889 B1 * 8/2011 Donaldson et al. 435/157

2002/0045786 A1 4/2002 Gammersbach et al.
2005/0054861 A1 3/2005 Manzer
2005/0089979 A1 4/2005 Ezeji et al.
2005/0112739 A1 5/2005 Golubkov
2005/0233423 A1 10/2005 Berka et al.
2007/0259411 A1 11/2007 Bramucci
2008/0131948 A1 6/2008 Manzer et al.
2008/0220488 A1 9/2008 D'Amore et al.
2014/0030794 A1 1/2014 Donaldson et al.

FOREIGN PATENT DOCUMENTS

EP 0088602 A2 9/1983
EP 0263403 A2 4/1988
EP 0263403 B1 4/1988
EP 0263403 A3 6/1990
EP 0263403 B1 4/1993
GB 576480 4/1946
GB 576480 A 4/1946
WO 9703932 A1 2/1997
WO 03031539 A1 4/2003

OTHER PUBLICATIONS

A. D. Petroff et al., De La Structure Du Di-Isobutylene De Malbot,
Bulletin De La Societe Chimique DE France, 1933, vol. 53:327-330.
Jean Baptiste Senderens: Chimique Organique. Deshydration
Catalytique, En Phase Gazeuse, Des Alcools Formeniques En Pres-
ence Des Bisulfates Alcalins, Comptes Rendus Hebdomadaires Des
Seances De L'Academie Des Sciences, 1930, vol. 190:1167-1170.
V. N. Ipatieff et al., The Dehydration of the Lower Aliphatic Alcohols
in the Presence of Dilute Aqueous Solutions of Acids and Salts,
Journal of the American Chemical Society, 1944, vol. 66:1627-1631.
Homer Adkins et al., Dehydration of Alcohols Over Alumina, Journal
of the American Chemical Society, 1925, vol. 47:1163-1167.
D. Fritsch et al., Application of a Forced-Flow Catalytic Membrane
Reactor for the Dimerisation of Isobutene, Catalysis Today, 2004,
vol. 98:295-308.
International Search Report Dated Feb. 5, 2008, International Appli-
cation No. PCT/US2007/014169, International Filing Date: Jun. 15,
2007.
Ernst Billig, Butyl Alcohols, Kirk-Othmer Encyclopedia of Chemi-
cal Tech., vol. 4, Published Online Apr. 16, 2001, pp. 393-402.
Liu et al., Separation and Purification Technology, vol. 42, 2005, pp.
273-282.

(Continued)

Primary Examiner — Rosalynd Keys

(57) **ABSTRACT**

The present invention relates to a catalytic process for making
isooctenes using a reactant comprising isobutanol and water.
The isooctenes so produced are useful for the production of
fuel additives.

17 Claims, 7 Drawing Sheets

(56)

References Cited**OTHER PUBLICATIONS**

- Zambonelli et al., *Current Microbiology*, vol. 23, 1991, pp. 281-283.
- Ingraham et al., *Archives of Biochemistry and Biophysics*, vol. 88, 1960, pp. 157-166.
- Examination of IPR 2014-00143; entitled Renewable Compositions; U.S. Pat. No. 8,378,160; including, but not limited to, Petition for Inter Partes Review filed Nov. 11, 2013.
- Examination of IPR 2014-00142; entitled Renewable Compositions; U.S. Pat. No. 8,193,402; including, but not limited to, Petition for Inter Partes Review filed Nov. 11, 2013.
- Examination of IPR 2014-00144; entitled Renewable Compositions; U.S. Pat. No. 8,487,149; including, but not limited to, Petition for Inter Partes Review filed Nov. 11, 2013.
- Prosecution of U.S. Appl. No. 11/586,315, filed Oct. 25, 2006 (U.S. Pat. No. 7,851,188), including, but not limited to, IPRs U.S. Appl. No. 95/001,718 and U.S. Appl. No. 95/001,857.
- Prosecution of U.S. Appl. No. 12/103,844, filed Apr. 16, 2008, (U.S. Pat. No. 7,910,342).
- Prosecution of U.S. Appl. No. 12/018,216, filed Jan. 23, 2008, (U.S. Pat. No. 7,993,889) including, but not limited to, IPRs U.S. Appl. No. 95/001,735 and U.S. Appl. No. 90/012,503.
- Prosecution of U.S. Appl. No. 13/205,351, filed Aug. 8, 2011, (U.S. Pat. No. 8,178,328) including, but not limited to, IPR U.S. Appl. No. 95/001,998.
- Prosecution of U.S. Appl. No. 12/966,333, filed Dec. 13, 2010, (U.S. Pat. No. 8,273,558).
- Prosecution of U.S. Appl. No. 12/939,284, filed Nov. 4, 2010, (U.S. Pat. No. 8,283,144).
- Prosecution of U.S. Appl. No. 13/539,125, filed Jun. 29, 2012.
- Prosecution of U.S. Appl. No. 13/646,097, filed Oct. 5, 2012.
- Prosecution of U.S. Appl. No. 12/939,315, filed Nov. 4, 2010.
- Zambonelli et al., "Autolysogeny and High Isobutyl Alcohol Production in *Saccharomyces cerevisiae*", *Current Microbiology*, vol. 23, 1991, pp. 281-283.
- Doherty et al., *Conceptual Design of Distillation Systems*, 2001, pp. 365-366, McGraw-Hill New York.
- Ramey et al., *Production of Butyric Acid and Butanol From Biomass*, Final Report of Work Performed Under U.S. Department of Energy DE-F-G02-00ER86106, 57-58, 2004, 103 pages.
- Prosecution of U.S. Appl. No. 13/839,246, U.S. Published Patent Application 2014/0030794, filed Mar. 15, 2013.
- Anderson et al., *Solid Acid and Base Catalysts, Catalysis: Science and Technology*, 1981, vol. 2, 232-273, Springer-Verlag, New York.
- Satterfield, C. N., "Catalyst Preparation and Manufacture", *Heterogeneous Catalysis in Practice*, 2.SUP.ED Edition, Chapter 4, 68-98, 1991, McGraw-Hill, New York.
- Perry et al., *Perry's Chemical Engineer's Handbook*, 7.SUP.ED Edition, Sections 13, 18, and 22, 1997, McGraw-Hill, New York.
- Augustine, R. L., "The Active Site", *Heterogeneous Catalysis for the Synthetic Chemist*, Section 3, 27-49, 1996, Marcel Dekker, New York.
- Mescheryakov et al., *Izvest Akad. Nauk S.S.S.R.*, 1950, 282-285.
- Liu et al., "Separation of acetone—butanol—ethanol (ABE) from dilute aqueous solutions by pervaporation", *Separation and Purification Technology*, 42, 2005, 273-282.
- Ingraham et al., "The Formation of Higher Aliphatic Alcohols by Mutant Strains of *Saccharomyces cerevisiae*" *Archives of Biochemistry and Biophysics*, vol. 88, 1960, 157-166.
- Kirk Othmer *Encyclopedia of Chemical Technology*, "Butyl Alcohols", vol. 4, Published Online Apr. 2001, 393-402.
- Adkins, H., "Dehydration of Alcohols Over Alumina", *Journal of the American Chemical Society*, vol. 47, 1925, 1163-1167.
- Senderens, J. B., *Chimie Organique. Deshydratation Catalytique, En Phase Gazeuse, Des Alcools Formeniques En Presence Des Bisulfates Alcalins, Comptes Rendus Hebdomadaires Des Seances De L'Academie Des Sciences*, vol. 190, 1930, 1167-1170.
- Prosecution of U.S. Appl. No. 13/838,949, U.S. Published Patent Application 2014/0051151, filed Mar. 15, 2013.

* cited by examiner

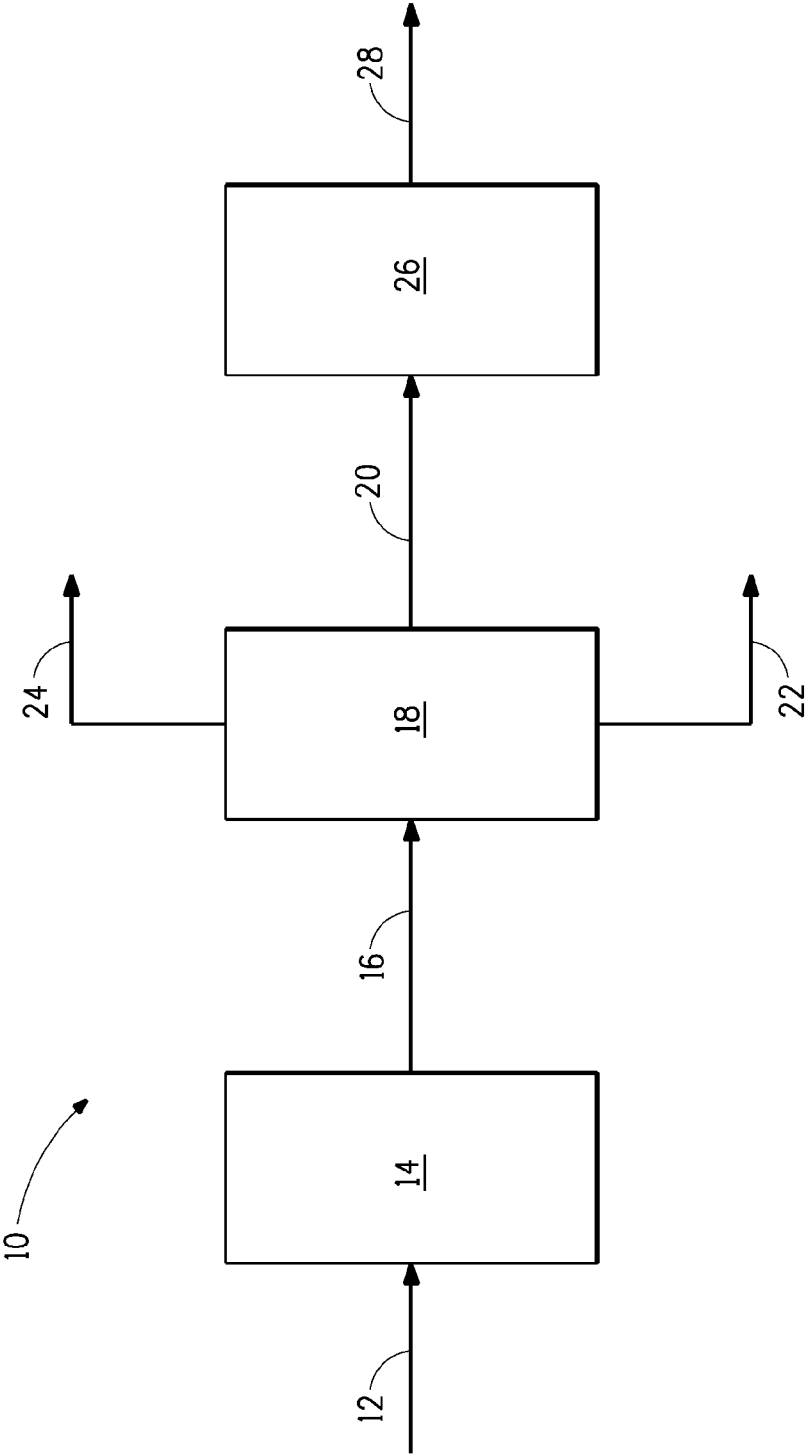


FIG. 1

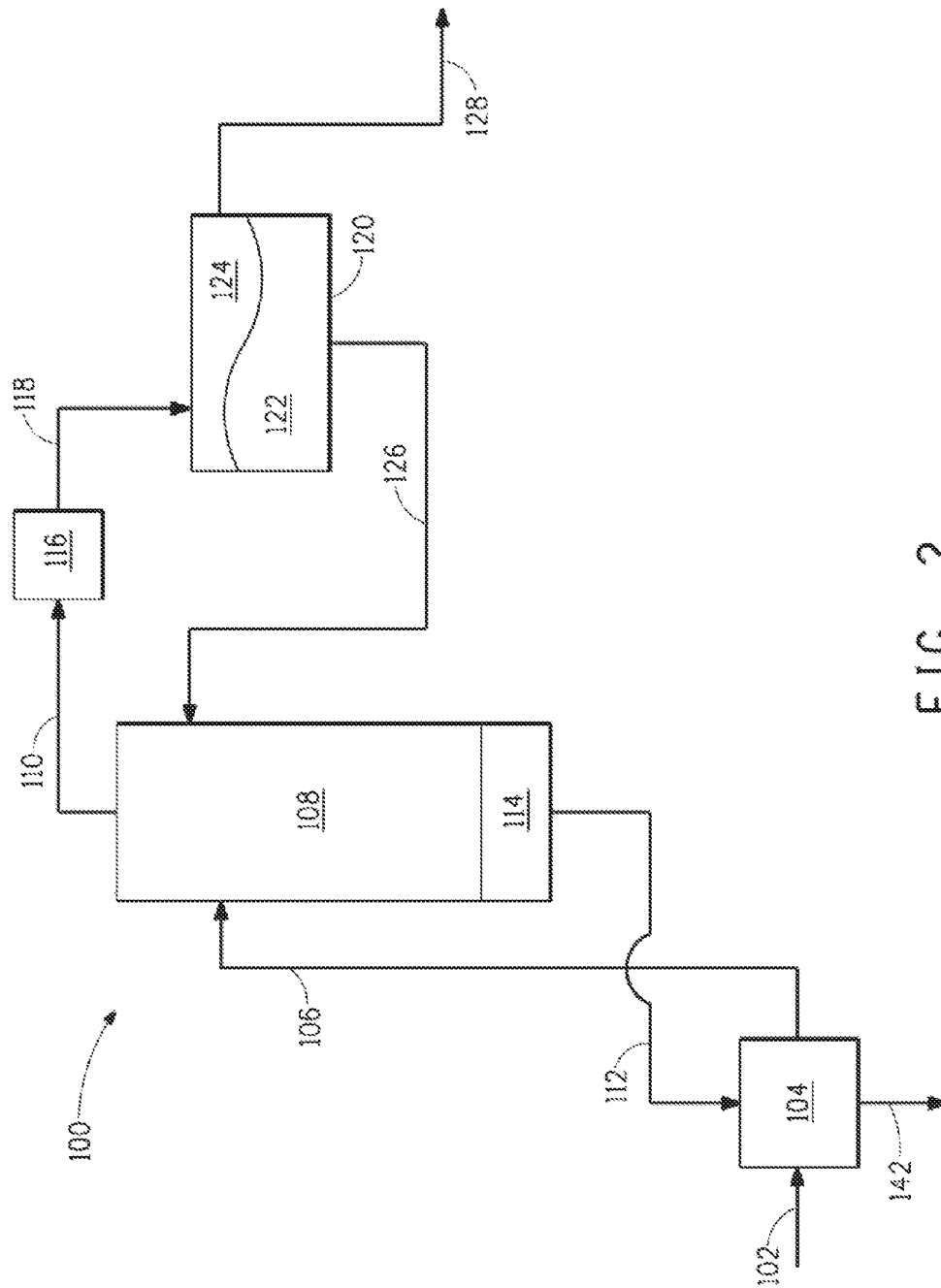


FIG. 2

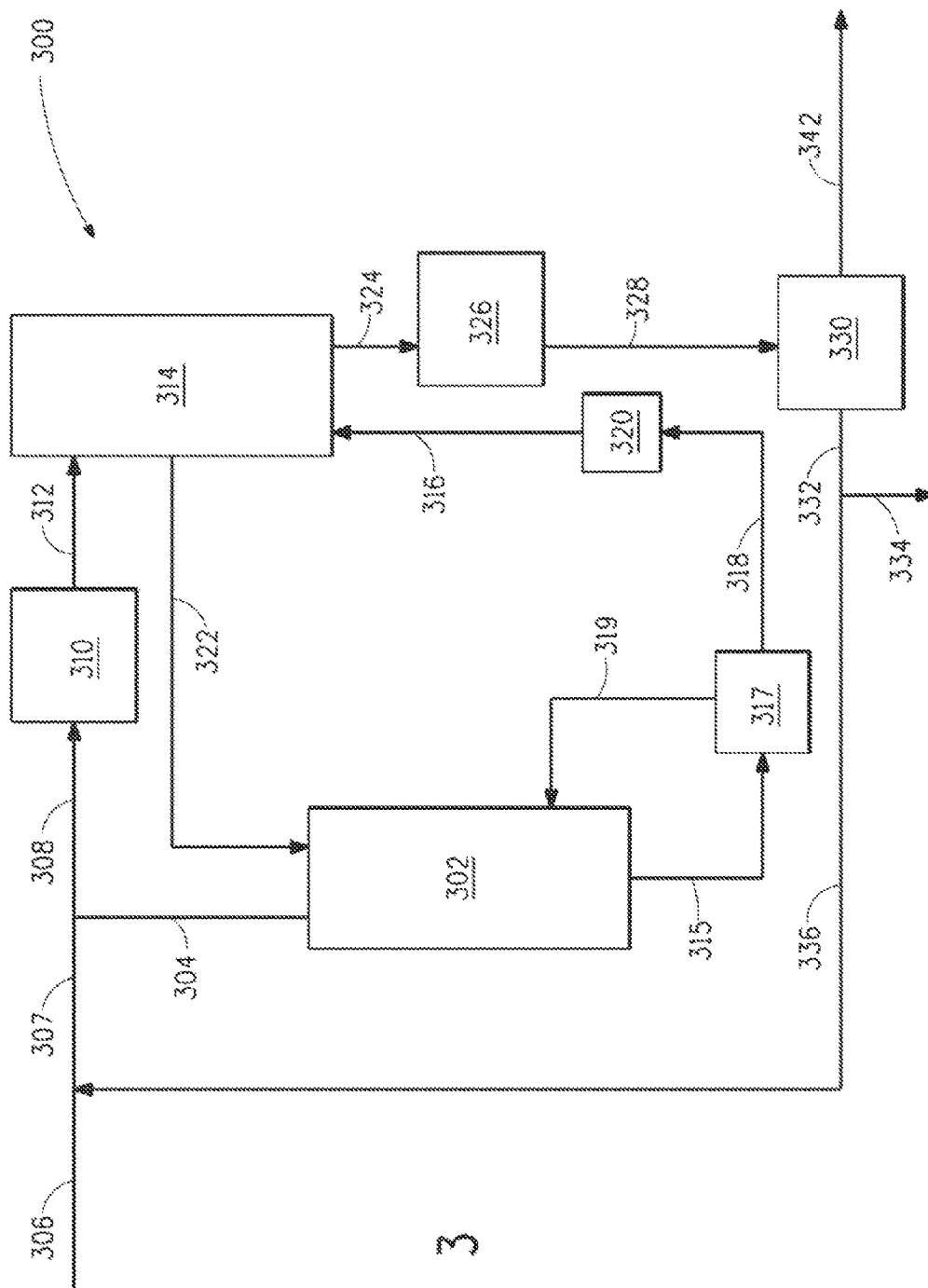


FIG. 3

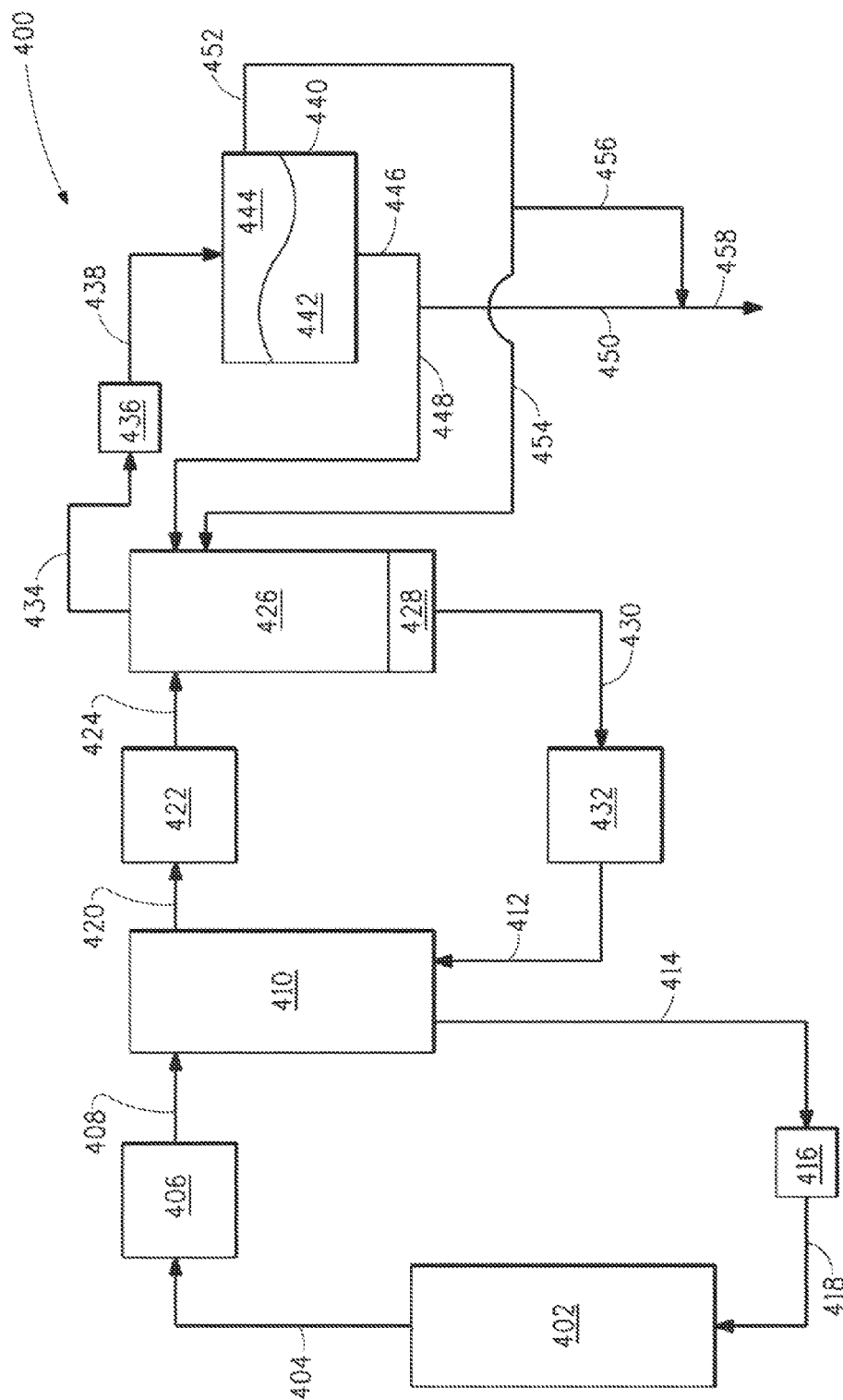


FIG. 4

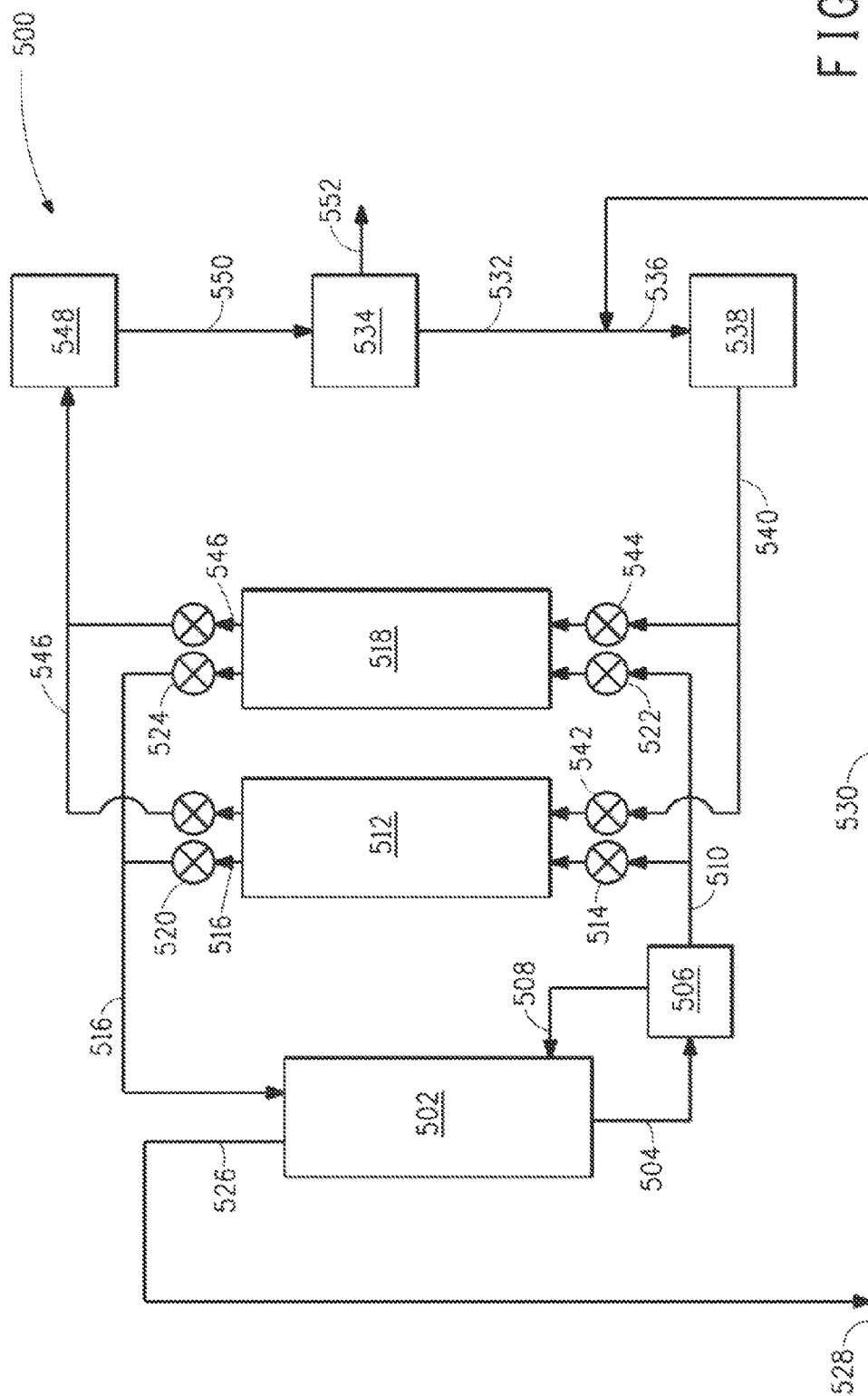


FIG. 5

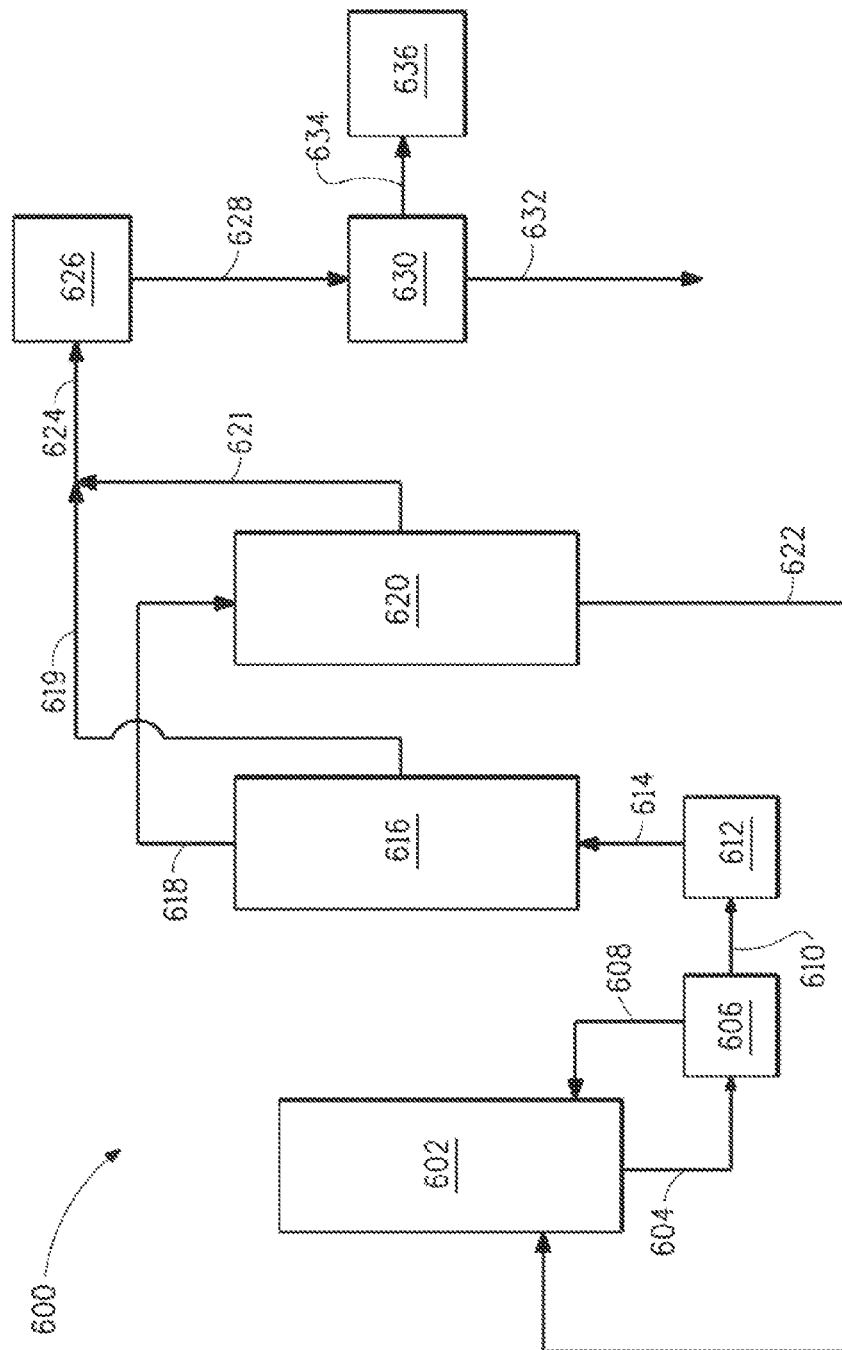


FIG. 6

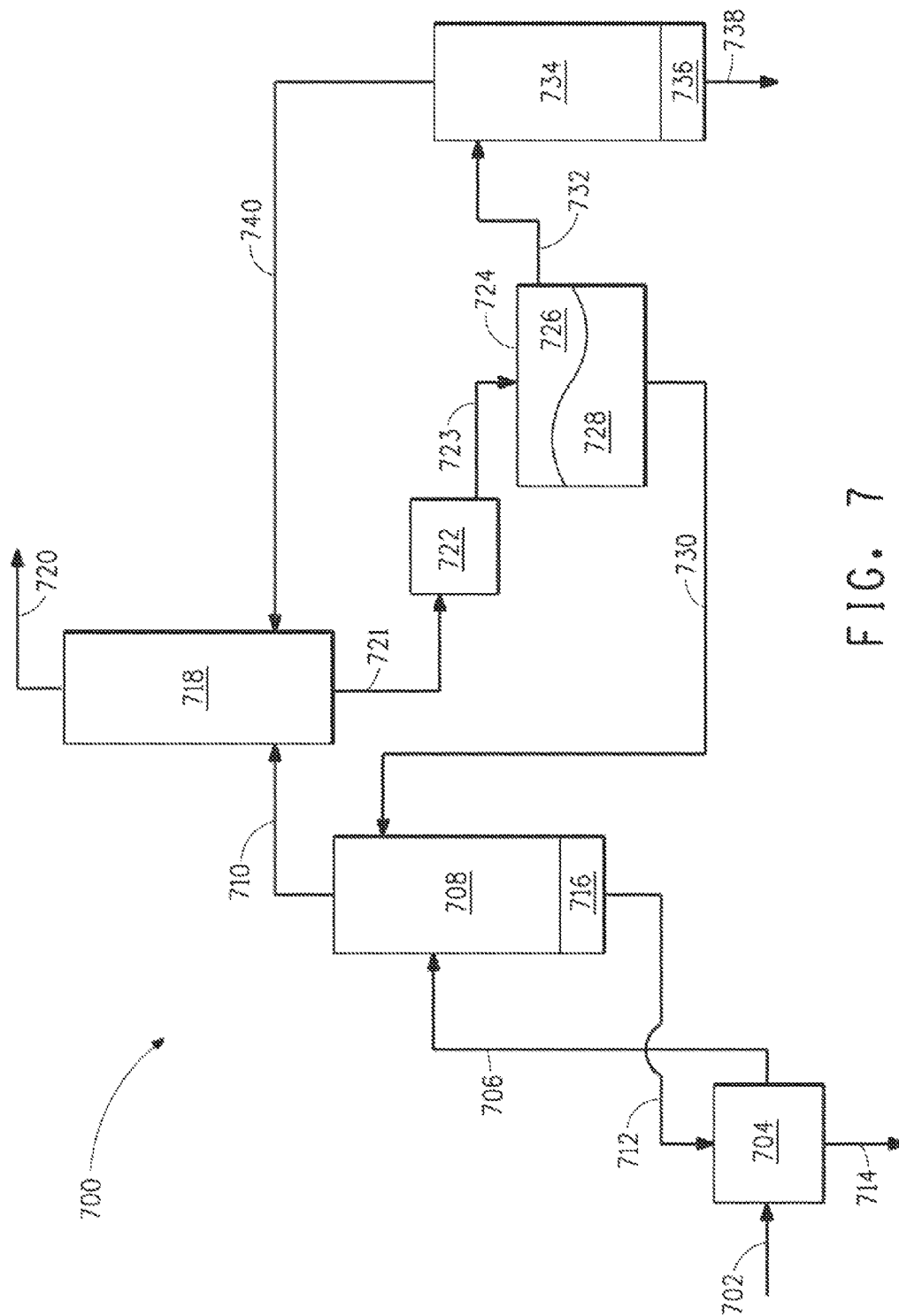


FIG. 7

1

PROCESS FOR MAKING ISOOCETENES FROM AQUEOUS ISOBUTANOL

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority under 35 U.S.C. §119 from U.S. Provisional Application Ser. No. 60/814,153 (filed Jun. 16, 2006), the disclosure of which is incorporated by reference herein for all purposes as if fully set forth.

FIELD OF INVENTION

The present invention relates to a process for making isoocetenes using aqueous isobutanol as a reactant.

BACKGROUND

Isoocetenes are useful intermediates for the production of fuel additives. Isoocetenes are typically produced from the reaction of isobutene or isobutene-containing hydrocarbon mixtures with an acid catalyst. U.S. Patent Application No. 2004/0054246, for example, describes the production of diisobutene from isobutene or mixtures comprising isobutenes using a solid acidic ion-exchange resin. U.S. Patent Application No. 2002/0045786 describes the preparation of diisobutylene from an isobutanol-containing raffinate using an acidic catalyst. Meshcheryakov, A. P., et al (Izvest. Akad. Nauk S.S.S.R. (1950) 282-285) describe the reaction of pure isobutanol in a sulfuric acid medium to produce di-

and triisobutylenes. Efforts directed at improving air quality and increasing energy production from renewable resources have resulted in renewed interest in alternative fuels, such as ethanol and butanol, that might replace gasoline and diesel fuel. Efforts are currently underway to increase the efficiency of isobutanol production by fermentative microorganisms with the expectation that renewable feedstocks, such as corn waste and sugar cane bagasse, could be used as carbon sources. It would be desirable to be able to utilize such isobutanol streams for the production of isoocetenes, and for the further production of fuel additives from said isoocetenes.

SUMMARY

The present invention relates to a process for making at least one isoocetene comprising contacting a reactant comprising isobutanol and at least about 5% water (by weight relative to the weight of the water plus isobutanol) with at least one acid catalyst at a temperature of about 50 degrees C. to about 450 degrees C. and a pressure from about 0.1 MPa to about 20.7 MPa to produce a reaction product comprising said at least one isoocetene, and recovering said at least one isoocetene from said reaction product to obtain at least one recovered isoocetene. In one embodiment, the reactant is obtained from fermentation broth.

The at least one recovered isoocetene is useful as an intermediate for the production of transportation fuels and fuel additives. In particular, the at least one recovered isoocetene can be converted to isoocetanes, isoocetanol or isoocetyl alkyl ethers.

BRIEF DESCRIPTION OF THE DRAWING

The Drawing consists of seven figures.

FIG. 1 illustrates an overall process useful for carrying out the present invention.

2

FIG. 2 illustrates a method for producing an isobutanol/water stream using distillation wherein fermentation broth comprising isobutanol, but being substantially free of acetone and ethanol, is used as the feed stream.

FIG. 3 illustrates a method for producing an isobutanol/water stream using gas stripping wherein fermentation broth comprising isobutanol and water is used as the feed stream.

FIG. 4 illustrates a method for producing an isobutanol/water stream using liquid-liquid extraction wherein fermentation broth comprising isobutanol and water is used as the feed stream.

FIG. 5 illustrates a method for producing an isobutanol/water stream using adsorption wherein fermentation broth comprising isobutanol and water is used as the feed stream.

FIG. 6 illustrates a method for producing an isobutanol/water stream using pervaporation wherein fermentation broth comprising isobutanol and water is used as the feed stream.

FIG. 7 illustrates a method for producing an isobutanol/water stream using distillation wherein fermentation broth comprising isobutanol and ethanol, but being substantially free of acetone, is used as the feed stream.

DETAILED DESCRIPTION

The present invention relates to a process for making at least one isoocetene from a reactant comprising water and isobutanol. The at least one isoocetene so produced is useful as an intermediate for the production of transportation fuels, wherein transportation fuels include, but are not limited to, gasoline, diesel fuel and jet fuel. The present invention further relates to the production of transportation fuel additives using isoocetenes produced by the process of the invention.

In its broadest embodiment, the process of the invention comprises contacting a reactant comprising isobutanol and water with at least one acid catalyst to produce a reaction product comprising at least one isoocetene, and recovering said at least one isoocetene from said reaction product to obtain at least one recovered isoocetene. By isoocetene is meant any olefin having eight carbons, wherein at least one of the carbons is a secondary or tertiary carbon.

Although the reactant could comprise less than about 5% water by weight relative to the weight of the water plus isobutanol, it is preferred that the reactant comprise at least about 5% water. In a more specific embodiment, the reactant comprises from about 5% to about 80% water by weight relative to the weight of the water plus isobutanol.

In one preferred embodiment, the reactant is derived from fermentation broth, and comprises at least about 50% isobutanol (by weight relative to the weight of the isobutanol plus water) (sometimes referred to herein as "aqueous isobutanol"). One advantage to the microbial (fermentative) production of isobutanol is the ability to utilize feedstocks derived from renewable sources, such as corn stalks, corn cobs, sugar cane, sugar beets or wheat, for the fermentation process. Efforts are currently underway to engineer (through recombinant means) or select for organisms that produce isobutanol with greater efficiency than is obtained with current microorganisms. Such efforts are expected to be successful, and the process of the present invention will be applicable to any fermentation process that produces isobutanol at levels currently seen with wild-type microorganisms, or with genetically modified microorganisms from which enhanced production of isobutanol is obtained.

Isobutanol can be fermentatively produced by recombinant microorganisms as described in copending and commonly owned U.S. Pat. No. 7,851,188, page 5, line 9 through page 45, line 20, including the sequence listing. The biosynthetic

pathway enables recombinant organisms to produce a fermentation product comprising isobutanol from a substrate such as glucose; in addition to isobutanol, ethanol is formed. The biosynthetic pathway enables recombinant organisms to produce isobutanol from a substrate such as glucose. The biosynthetic pathway to isobutanol comprises the following substrate to product conversions:

- a) pyruvate to acetolactate, as catalyzed for example by acetolactate synthase encoded by the gene given as SEQ ID NO:19;
- b) acetolactate to 2,3-dihydroxyisovalerate, as catalyzed for example by acetohydroxy acid isomeroreductase encoded by the gene given as SEQ ID NO:31;
- c) 2,3-dihydroxyisovalerate to α -ketoisovalerate, as catalyzed for example by acetohydroxy acid dehydratase encoded by the gene given as SEQ ID NO:33;
- d) α -ketoisovalerate to isobutyraldehyde, as catalyzed for example by a branched-chain keto acid decarboxylase encoded by the gene given as SEQ ID NO:35; and
- e) isobutyraldehyde to isobutanol, as catalyzed for example by a branched-chain alcohol dehydrogenase encoded by the gene given as SEQ ID NO:37.

Methods for generating recombinant microorganisms, including isolating genes, constructing vectors, transforming hosts, and analyzing expression of genes of the biosynthetic pathway are described in detail by Maggio-Hall, et al. in U.S. Pat. No. 7,851,188.

The biological production of butanol by microorganisms is believed to be limited by butanol toxicity to the host organism. Copending and commonly owned U.S. Pat. No. 7,659,104, page 5, line 1 through page 36, Table 5, and including the sequence listing (filed 4 May 2006) enables a method for selecting for microorganisms having enhanced tolerance to butanol, wherein "butanol" refers to 1-butanol, 2-butanol, isobutanol or combinations thereof. A method is provided for the isolation of a butanol tolerant microorganism comprising:

- a) providing a microbial sample comprising a microbial consortium;
- b) contacting the microbial consortium in a growth medium comprising a fermentable carbon source until the members of the microbial consortium are growing;
- c) contacting the growing microbial consortium of step (b) with butanol; and
- d) isolating the viable members of step (c) wherein a butanol tolerant microorganism is isolated.

The method of U.S. Pat. No. 7,659,104 can be used to isolate microorganisms tolerant to isobutanol at levels greater than 1% weight per volume.

Fermentation methodology is well known in the art, and can be carried out in a batch-wise, continuous or semi-continuous manner. As is well known to those skilled in the art, the concentration of isobutanol in the fermentation broth produced by any process will depend on the microbial strain and the conditions, such as temperature, growth medium, mixing and substrate, under which the microorganism is grown.

Following fermentation, the fermentation broth from the fermentor can be used for the process of the invention. In one preferred embodiment the fermentation broth is subjected to a refining process to produce an aqueous stream comprising an enriched concentration of isobutanol. By "refining process" is meant a process comprising one unit operation or a series of unit operations that allows for the purification of an impure aqueous stream comprising isobutanol to yield an aqueous stream comprising substantially pure isobutanol. For example, in one embodiment, the refining process yields a stream that comprises at least about 5% water and isobutanol,

but is substantially free of ethanol and/or acetone that may have been present in the fermentation broth.

Refining processes typically utilize one or more distillation steps as a means for recovering a fermentation product. It is expected, however, that fermentative processes will produce isobutanol at very low concentrations relative to the concentration of water in the fermentation broth. This can lead to large capital and energy expenditures to recover the isobutanol by distillation alone. As such, other techniques can be used either alone or in combination with distillation as a means of concentrating the dilute isobutanol product. In such processes where separation techniques are integrated with the fermentation step, cells are often removed from the stream to be refined by centrifugation or membrane separation techniques, yielding a clarified fermentation broth. These cells are then returned to the fermentor to improve the productivity of the isobutanol fermentation process. The clarified fermentation broth is then subjected to such techniques as pervaporation, gas stripping, liquid-liquid extraction, perstraction, adsorption, distillation, or combinations thereof. Depending on product mix, these techniques can provide a stream comprising water and isobutanol suitable for use in the process of the invention. If further purification is necessary, the stream can be treated further by distillation to yield an aqueous isobutanol stream.

Separation Similarities of 1-Butanol and Isobutanol

1-Butanol and isobutanol share many common features that allow the separation schemes devised for the separation of 1-butanol and water to be applicable to the isobutanol and water system. For instance both 1-butanol and isobutanol are equally hydrophobic molecules possessing log Kow coefficients of 0.88 and 0.83, respectively. Kow is the partition coefficient of a species at equilibrium in an octanol-water system. Based on the similarities of the hydrophobic nature of the two molecules one would expect both molecules to partition in largely the same manner when exposed to various solvent systems such as decanol or when adsorbed onto various solid phases such as silicone or silicalite. In addition, both 1-butanol and isobutanol share similar K values, or vapor-liquid partition coefficients, when in solution with water. Another useful thermodynamic term is α which is the ratio of partition coefficients, K values, for a given binary system. For a given concentration and temperature up to 100° C. the values for K and α are nearly identical for 1-butanol and isobutanol in their respective butanol-water systems, indicating that in evaporation type separation schemes such as gas stripping, pervaporation, and distillation, both molecules should perform equivalently.

The separation of 1-butanol from water, and the separation of 1-butanol from a mixture of acetone, ethanol, 1-butanol and water as part of the ABE fermentation process by distillation have been described. In particular, in a butanol and water system, 1-butanol forms a low boiling heterogeneous azeotrope in equilibrium with 2 liquid phases comprised of 1-butanol and water. This azeotrope is formed at a vapor phase composition of approximately 58% by weight 1-butanol (relative to the weight of water plus 1-butanol) when the system is at atmospheric pressure (as described by Doherty, M. F. and Malone, M. F. in *Conceptual Design of Distillation Systems* (2001), Chapter 8, pages 365-366, McGraw-Hill, New York). The liquid phases are roughly 6% by weight 1-butanol (relative to the weight of water plus 1-butanol) and 80% by weight 1-butanol (relative to the weight of water plus 1-butanol), respectively. In similar fashion, isobutanol also forms a minimum boiling heterogeneous azeotrope with water that is in equilibrium with two liquid phases. The azeotrope is formed at a vapor phase composition of 67% by

5

weight isobutanol (relative to the weight of water plus isobutanol) (as described by Doherty, M. F. and Malone, M. F. in *Conceptual Design of Distillation Systems* (2001), Chapter 8, pages 365-366, McGraw-Hill, New York). The two liquid phases are roughly 6% by weight isobutanol (relative to the weight of water plus isobutanol) and 80% by weight isobutanol (relative to the weight of water plus isobutanol), respectively. Thus, in the process of distillative separation of a dilute 1-butanol and water or isobutanol and water system, a simple procedure of sub-cooling the azeotrope composition into the two phase region allows one to cross the distillation boundary formed by the azeotrope.

Distillation

For fermentation processes in which isobutanol is the predominant alcohol, aqueous isobutanol can be recovered by azeotropic distillation, as described generally in Ramey, D. and Yang, S.-T. (*Production of butyric acid and butanol from biomass*, Final Report of work performed under U. S. Department of Energy DE-F-G02-00ER86106, pages 57-58) for the production of 1-butanol. An aqueous isobutanol stream from the fermentation broth is fed to a distillation column, from which an isobutanol-water azeotrope is removed as a vapor phase. The vapor phase from the distillation column (comprising at least about 33% water (by weight relative to the weight of water plus isobutanol)) can then be used directly as the reactant for the process of the present invention, or can be fed to a condenser. Upon cooling, an isobutanol-rich phase (comprising at least about 16% water (relative to the weight of water plus isobutanol)) will separate from a water-rich phase in the condenser. One skilled in the art will know that solubility is a function of temperature, and that the actual concentration of water in the aqueous isobutanol stream will vary with temperature. The isobutanol-rich phase can be decanted and used for the process of the invention, and the water-rich phase preferably is returned to the distillation column.

For fermentation processes in which an aqueous stream comprising isobutanol and ethanol are produced, the aqueous isobutanol/ethanol stream is fed to a distillation column, from which a ternary isobutanol/ethanol/water azeotrope is removed. The azeotrope of isobutanol, ethanol and water is fed to a second distillation column from which an ethanol/water azeotrope is removed as an overhead stream. A stream comprising isobutanol, water and some ethanol is then cooled and fed to a decanter to form an isobutanol-rich phase and a water-rich phase. The isobutanol-rich phase is fed to a third distillation column to separate an isobutanol/water stream from an ethanol/water stream. The isobutanol/water stream can be used for the process of the invention.

Pervaporation

Generally, there are two steps involved in the removal of volatile components by pervaporation. One is the sorption of the volatile component into the membrane, and the other is the diffusion of the volatile component through the membrane due to a concentration gradient. The concentration gradient is created either by a vacuum applied to the opposite side of the membrane or through the use of a sweep gas, such as air or carbon dioxide, also applied along the backside of the membrane. Pervaporation for the separation of 1-butanol from a fermentation broth has been described by Meagher, M. M., et al in U.S. Pat. No. 5,755,967 (Column 5, line 20 through Column 20, line 59) and by Liu, F., et al (*Separation and Purification Technology* (2005) 42:273-282). According to U.S. Pat. No. 5,755,967, acetone and/or 1-butanol were selectively removed from an ABE fermentation broth using a pervaporation membrane comprising silicalite particles embedded in a polymer matrix. Examples of polymers include polydimethylsiloxane and cellulose acetate, and vacuum was

6

used as the means to create the concentration gradient. The method of U.S. Pat. No. 5,755,967 can similarly be used to recover a stream comprising isobutanol and water from fermentation broth, and this stream can be used directly as the reactant of the present invention, or can be further treated by distillation to produce an aqueous isobutanol stream that can be used as the reactant of the present invention.

Gas Stripping

In general, gas stripping refers to the removal of volatile compounds, such as butanol, from fermentation broth by passing a flow of stripping gas, such as carbon dioxide, helium, hydrogen, nitrogen, or mixtures thereof, through the fermentor culture or through an external stripping column to form an enriched stripping gas. Gas stripping to remove 1-butanol from an ABE fermentation has been exemplified by Ezeji, T., et al (U.S. Patent Application No. 2005/0089979, paragraphs 16 through 84). According to U.S. 2005/0089979, a stripping gas (carbon dioxide and hydrogen) was fed into a fermentor via a sparger. The flow rate of the stripping gas through the fermentor was controlled to give the desired level of solvent removal. The flow rate of the stripping gas is dependent on such factors as configuration of the system, cell concentration and solvent concentration in the fermentor. This process can also be used to produce an enriched stripping gas comprising isobutanol and water, and this stream can be used directly as the reactant of the present invention, or can be further treated by distillation to produce an aqueous isobutanol stream that can be used as the reactant of the present invention.

Adsorption

Using adsorption, organic compounds of interest are removed from dilute aqueous solutions by selective sorption of the organic compound by a sorbent, such as a resin. Feldman, J. in U.S. Pat. No. 4,450,294 (Column 3, line 45 through Column 9, line 40 (Example 6)) describes the recovery of an oxygenated organic compound from a dilute aqueous solution with a cross-linked polyvinylpyridine resin or nuclear substituted derivative thereof. Suitable oxygenated organic compounds included ethanol, acetone, acetic acid, butyric acid, n-propanol and n-butanol. The adsorbed compound was desorbed using a hot inert gas such as carbon dioxide. This process can also be used to recover an aqueous stream comprising desorbed isobutanol, and this stream can be used directly as the reactant of the present invention, or can be further treated by distillation to produce an aqueous isobutanol stream that can be used as the reactant of the present invention.

Liquid-Liquid Extraction

Liquid-liquid extraction is a mass transfer operation in which a liquid solution (the feed) is contacted with an immiscible or nearly immiscible liquid (solvent) that exhibits preferential affinity or selectivity towards one or more of the components in the feed, allowing selective separation of said one or more components from the feed. The solvent comprising the one or more feed components can then be separated, if necessary, from the components by standard techniques, such as distillation or evaporation. One example of the use of liquid-liquid extraction for the separation of butyric acid and butanol from microbial fermentation broth has been described by Cenedella, R. J. in U.S. Pat. No. 4,628,116 (Column 2, line 28 through Column 8, line 57). According to U.S. Pat. No. 4,628,116, fermentation broth containing butyric acid and/or butanol was acidified to a pH from about 4 to about 3.5, and the acidified fermentation broth was then introduced into the bottom of a series of extraction columns containing vinyl bromide as the solvent. The aqueous fermentation broth, being less dense than the vinyl bromide, floated

to the top of the column and was drawn off. Any butyric acid and/or butanol present in the fermentation broth was extracted into the vinyl bromide in the column. The column was then drawn down, the vinyl bromide was evaporated, resulting in purified butyric acid and/or butanol.

Other solvent systems for liquid-liquid extraction, such as decanol, have been described by Roffler, S. R., et al. (Bioprocess Eng. (1987) 1:1-12) and Taya, M., et al. (J. Ferment. Technol. (1985) 63:181). In these systems, two phases were formed after the extraction: an upper less dense phase comprising decanol, 1-butanol and water, and a more dense phase comprising mainly decanol and water. Aqueous 1-butanol was recovered from the less dense phase by distillation.

These processes can also be used to obtain an aqueous stream comprising isobutanol that can be used directly as the reactant of the present invention, or can be further treated by distillation to produce an aqueous isobutanol stream that can be used as the reactant of the present invention.

Aqueous streams comprising isobutanol, as obtained by any of the methods above, can be the reactant for the process of the present invention. The reaction to form at least one isooctene is performed at a temperature of from about 50 degrees Centigrade to about 450 degrees Centigrade. In a more specific embodiment, the temperature is from about 100 degrees Centigrade to about 250 degrees Centigrade.

The reaction can be carried out under an inert atmosphere at a pressure of from about atmospheric pressure (about 0.1 MPa) to about 20.7 MPa. In a more specific embodiment, the pressure is from about 0.1 MPa to about 3.45 MPa. Suitable inert gases include nitrogen, argon and helium.

The reaction can be carried out in liquid or vapor phase and can be run in either batch or continuous mode as described, for example, in H. Scott Fogler, (*Elements of Chemical Reaction Engineering*, 2nd Edition, (1992) Prentice-Hall Inc, Calif.).

The at least one acid catalyst can be a homogeneous or heterogeneous catalyst. Homogeneous catalysis is catalysis in which all reactants and the catalyst are molecularly dispersed in one phase. Homogeneous acid catalysts include, but are not limited to inorganic acids, organic sulfonic acids, heteropolyacids, fluoroalkyl sulfonic acids, metal sulfonates, metal trifluoroacetates, compounds thereof and combinations thereof. Examples of homogeneous acid catalysts include sulfuric acid, fluorosulfonic acid, phosphoric acid, p-toluene-sulfonic acid, benzenesulfonic acid, hydrogen fluoride, phosphotungstic acid, phosphomolybdic acid, and trifluoromethanesulfonic acid.

Heterogeneous catalysis refers to catalysis in which the catalyst constitutes a separate phase from the reactants and products. Heterogeneous acid catalysts include, but are not limited to 1) heterogeneous heteropolyacids (HPAs), 2) natural clay minerals, such as those containing alumina or silica, 3) cation exchange resins, 4) metal oxides, 5) mixed metal oxides, 6) metal salts such as metal sulfides, metal sulfates, metal sulfonates, metal nitrates, metal phosphates, metal phosphonates, metal molybdates, metal tungstates, metal borates, 7) zeolites, and 8) combinations of groups 1-7. See, for example, Solid Acid and Base Catalysts, pages 231-273 (Tanabe, K., in *Catalysis: Science and Technology*, Anderson, J. and Boudart, M (eds.) 1981 Springer-Verlag, New York) for a description of solid catalysts.

The heterogeneous acid catalyst may also be supported on a catalyst support. A support is a material on which the acid catalyst is dispersed. Catalyst supports are well known in the art and are described, for example, in Satterfield, C. N. (*Heterogeneous Catalysis in Industrial Practice*, 2nd Edition, Chapter 4 (1991) McGraw-Hill, New York).

In one embodiment of the invention, the reaction is carried out using a heterogeneous catalyst, and the temperature and pressure are chosen so as to maintain the reactant and reaction product in the vapor phase. In a more specific embodiment, the reactant is obtained from a fermentation broth that is subjected to distillation to produce a vapor phase having at least about 33% water. The vapor phase is directly used as a reactant in a vapor phase reaction in which the acid catalyst is a heterogeneous catalyst, and the temperature and pressure are chosen so as to maintain the reactant and reaction product in the vapor phase. It is believed that this vapor phase reaction would be economically desirable because the vapor phase is not first cooled to a liquid prior to performing the reaction.

One skilled in the art will know that conditions, such as temperature, catalytic metal, support, reactor configuration and time can affect the reaction kinetics, product yield and product selectivity. Depending on the reaction conditions, such as the particular catalyst used, products other than isooctenes may be produced when isobutanol is contacted with an acid catalyst. Additional products comprise dibutyl ethers (such as di-1-butyl ether) and butenes. Standard experimentation, performed as described in the Examples herein, can be used to optimize the yield of isooctenes from the reaction.

Following the reaction, if necessary, the catalyst can be separated from the reaction product by any suitable technique known to those skilled in the art, such as decantation, filtration, extraction or membrane separation (see Perry, R. H. and Green, D. W. (eds), *Perry's Chemical Engineer's Handbook*, 7th Edition, Section 13, 1997, McGraw-Hill, New York, Sections 18 and 22).

The at least one isooctene can be recovered from the reaction product by distillation as described in Seader, J. D., et al (Distillation, in Perry, R. H. and Green, D. W. (eds), *Perry's Chemical Engineer's Handbook*, 7th Edition, Section 13, 1997, McGraw-Hill, New York). Alternatively, the at least one isooctene can be recovered by phase separation, or extraction with a suitable solvent, such as trimethylpentane or octane, as is well known in the art. Unreacted isobutanol can be recovered following separation of the at least one isooctene and used in subsequent reactions.

The present process and certain embodiments for accomplishing it are shown in greater detail in the Drawing figures.

Referring now to FIG. 1, there is shown a block diagram illustrating in a very general way apparatus 10 for deriving isooctenes from aqueous isobutanol produced by fermentation. An aqueous stream 12 of biomass-derived carbohydrates is introduced into a fermentor 14. The fermentor 14 contains at least one microorganism (not shown) capable of fermenting the carbohydrates to produce a fermentation broth that comprises isobutanol and water. A stream 16 of the fermentation broth is introduced into refining apparatus 18 in order to make a stream of aqueous isobutanol. The aqueous isobutanol is removed from the refining apparatus 18 as stream 20. Some water is removed from the refining apparatus 18 as stream 22. Other organic components present in the fermentation broth may be removed as stream 24. The aqueous isobutanol stream 20 is introduced into reaction vessel 26 containing an acid catalyst (not shown) capable of converting the isobutanol into a reaction product comprising at least one isooctene. The reaction product is removed as stream 28.

Referring now to FIG. 2, there is shown a block diagram for refining apparatus 100, suitable for producing an aqueous isobutanol stream, when the fermentation broth comprises isobutanol and water, and is substantially free of ethanol. A stream 102 of fermentation broth is introduced into a feed preheater 104 to raise the broth to a temperature of approxi-

mately 95° C. to produce a heated feed stream **106** which is introduced into a beer column **108**. The design of the beer column **108** needs to have a sufficient number of theoretical stages to cause separation of isobutanol from water such that an isobutanol/water azeotrope can be removed as a vaporous isobutanol/water azeotrope overhead stream **110** and hot water as a bottoms stream **112**. Bottoms stream **112**, is used to supply heat to feed preheater **104** and leaves feed preheater **104** as a lower temperature bottoms stream **142**. Reboiler **114** is used to supply heat to beer column **108**. Vaporous isobutanol/water azeotrope overhead stream **110** is roughly 67% by weight isobutanol of the total isobutanol and water stream. This is the first opportunity by which a concentrated and partially purified isobutanol and water stream could be obtained; this partially purified isobutanol and water stream can be used as the feed stream to a reaction vessel (not shown) in which the aqueous isobutanol is catalytically converted to a reaction product that comprises at least one isoootene. Vaporous isobutanol/water azeotrope stream **110** can be fed to a condenser **116**, which lowers the stream temperature causing the vaporous isobutanol/water azeotrope overhead stream **110** to condense into a biphasic liquid stream **118**, which is introduced into decanter **120**. Decanter **120** will contain a lower phase **122** that is approximately 94% by weight water and approximately 6% by weight isobutanol and an upper phase **124** that is around 80% by weight isobutanol and 20% by weight water. A reflux stream **126** of lower phase **122** is introduced near the top of beer column **108**. A stream **128** of upper phase **124** can then be used as the feed stream to a reaction vessel (not shown) in which the aqueous isobutanol is catalytically converted to a reaction product that comprises at least one isoootene.

Referring now to FIG. 3, there is shown a block diagram for refining apparatus **300**, suitable for producing an aqueous isobutanol stream when the fermentation broth comprises isobutanol and water, and may additionally comprise ethanol. Fermentor **302** contains a fermentation broth comprising liquid isobutanol and water and a gas phase comprising CO₂ and to a lesser extent some vaporous isobutanol and water. Both phases may additionally comprise ethanol. A CO₂ stream **304** is then mixed with combined CO₂ stream **307** to give second combined CO₂ stream **308**. Second combined CO₂ stream **308** is then fed to heater **310** and heated to 60° C. to give heated CO₂ stream **312**. Heated CO₂ stream is then fed to gas stripping column **314** where it is brought into contact with heated clarified fermentation broth stream **316**. Heated clarified fermentation broth stream **316** is obtained as a clarified fermentation broth stream **318** from cell separator **317** and heated to 50° C. in heater **320**. Clarified fermentation broth stream **318** is obtained following separation of cells in cell separator **317**. Also leaving cell separator **317** is concentrated cell stream **319** which is recycled directly to fermentor **302**. The feed stream **315** to cell separator **317** comprises the liquid phase of fermentor **302**. Gas stripping column **314** contains a sufficient number of theoretical stages necessary to effect the transfer of isobutanol from the liquid phase to the gas phase. The number of theoretical stages is dependent on the contents of both streams **312** and **316**, as well as their flow rates and temperatures. Leaving gas stripping column **314** is an isobutanol depleted clarified fermentation broth stream **322** that is recirculated to fermentor **302**. An isobutanol enriched gas stream **324** leaving gas stripping column **314** is then fed to compressor **326**. Following compression, a compressed gas stream comprising isobutanol **328** is then fed to condenser **330** where the isobutanol in the gas stream is condensed into a liquid phase that is separate from non-condensable components in the stream **328**. Leaving the

condenser **330** is isobutanol depleted gas stream **332**. A first portion of gas stream **332** is bled from the system as bleed gas stream **334**, and the remaining second portion of isobutanol depleted gas stream **332**, stream **336**, is then mixed with makeup CO₂ gas stream **306** to form combined CO₂ gas stream **307**. The condensed isobutanol phase in condenser **330** leaves as aqueous isobutanol stream **342** and can be used as the feed to a distillation apparatus that is capable of separating aqueous isobutanol from ethanol, or can be used directly as a feed to a reaction vessel (not shown) in which the aqueous isobutanol is catalytically converted to a reaction product that comprises at least one isoootene.

Referring now to FIG. 4, there is shown a block diagram for refining apparatus **400**, suitable for producing an aqueous isobutanol stream, when the fermentation broth comprises isobutanol and water, and may additionally comprise ethanol. Fermentor **402** contains a fermentation broth comprising isobutanol and water and a gas phase comprising CO₂ and to a lesser extent some vaporous isobutanol and water. Both phases may additionally comprise ethanol. A stream **404** of fermentation broth is introduced into a feed preheater **406** to raise the broth temperature to produce a heated fermentation broth stream **408** which is introduced into solvent extractor **410**. In solvent extractor **410**, heated fermentation broth stream **408** is brought into contact with cooled solvent stream **412**, the solvent used in this case being decanol. Leaving solvent extractor **410**, is raffinate stream **414** that is depleted in isobutanol. Raffinate stream **414** is introduced into raffinate cooler **416** where it is lowered in temperature and returned to fermentor **402** as cooled raffinate stream **418**. Also leaving solvent extractor **410** is extract stream **420** that contains solvent, isobutanol and water. Extract stream **420** is introduced into solvent heater **422** where it is heated. Heated extract stream **424** is then introduced into solvent recovery distillation column **426** where the solvent is caused to separate from the isobutanol and water. Solvent column **426** is equipped with reboiler **428** necessary to supply heat to solvent column **426**. Leaving the bottom of solvent column **426** is solvent stream **430**. Solvent stream **430** is then introduced into solvent cooler **432** where it is cooled to 50° C. Cooled solvent stream **412** leaves solvent cooler **432** and is returned to extractor **410**. Leaving the top of solvent column **426** is solvent overhead stream **434** that contains an azeotropic mixture of isobutanol and water with trace amounts of solvent. This represents the first substantially concentrated and partially purified isobutanol/water stream that could fed to a reaction vessel (not shown) for catalytically converting the isobutanol to a reaction product that comprises at least one isoootene. Optionally, solvent overhead stream **434** could be fed into condenser **436** where the vaporous solvent overhead stream is caused to condense into a biphasic liquid stream **438** and introduced into decanter **440**. Decanter **440** will contain a lower phase **442** that is approximately 94% by weight water and approximately 6% by weight isobutanol and an upper phase **444** that is around 80% by weight isobutanol and 20% by weight water and a small amount of solvent. The lower phase **442** of decanter **440** leaves decanter **440** as water rich stream **446**. Water rich stream **446** is then split into two fractions. A first fraction of water rich stream **446** is returned as water rich reflux stream **448** to solvent column **426**. A second fraction of water rich stream **446**, water rich product stream **450**, is sent on to be mixed with isobutanol rich stream **456**. A stream **452** of upper phase **444** is split into two streams. Stream **454** is fed to solvent column **426** to be used as reflux. Stream **456** is combined with stream **450** to produce product stream **458**. Product stream **458** can be introduced as the feed to a distillation apparatus that is capable of separating

11

aqueous isobutanol from ethanol or can be used directly as a feed to a reaction vessel (not shown) in which the aqueous isobutanol is catalytically converted to a reaction product that comprises at least one isooctene.

Referring now to FIG. 5, there is shown a block diagram for refining apparatus 500, suitable for concentrating isobutanol, when the fermentation broth comprises isobutanol and water, and may additionally comprise ethanol. Fermentor 502 contains a fermentation broth comprising isobutanol and water and a gas phase comprising CO₂ and to a lesser extent some vaporous isobutanol and water. Both phases may additionally comprise ethanol. An isobutanol-containing fermentation broth stream 504 leaving fermentor 502 is introduced into cell separator 506. Cell separator 506 can be comprised of centrifuges or membrane units to accomplish the separation of cells from the fermentation broth. Leaving cell separator 506 is cell-containing stream 508 which is recycled back to fermentor 502. Also leaving cell separator 506 is clarified fermentation broth stream 510. Clarified fermentation broth stream 510 is then introduced into one or a series of adsorption columns 512 where the isobutanol is preferentially removed from the liquid stream and adsorbed on the solid phase adsorbent (not shown). Diagrammatically, this is shown in FIG. 5 as a two adsorption column system, although more or fewer columns could be used. The flow of clarified fermentation broth stream 510 is directed to the appropriate adsorption column 512 through the use of switching valve 514. Leaving the top of adsorption column 512 is isobutanol depleted stream 516 which passes through switching valve 520 and is returned to fermentor 502. When adsorption column 512 reaches capacity, as evidenced by an increase in the isobutanol concentration of the isobutanol depleted stream 516, flow of clarified fermentation broth stream 510 is then directed through switching valve 522 by closing switching valve 514. This causes the flow of clarified fermentation broth stream 510 to enter second adsorption column 518 where the isobutanol is adsorbed onto the adsorbent (not shown). Leaving the top of second adsorption column 518 is an isobutanol depleted stream which is essentially the same as isobutanol depleted stream 516. Switching valves 520 and 524 perform the function to divert flow of depleted isobutanol stream 516 from returning to one of the other columns that is currently being desorbed. When either adsorption column 512 or second adsorption column 518 reaches capacity, the isobutanol and water adsorbed into the pores of the adsorbent must be removed. This is accomplished using a heated gas stream to effect desorption of adsorbed isobutanol and water. The CO₂ stream 526 leaving fermentor 502 is first mixed with makeup gas stream 528 to produce combined gas stream 530. Combined gas stream 530 is then mixed with the cooled gas stream 532 leaving decanter 534 to form second combined gas stream 536. Second combined gas stream 536 is then fed to heater 538. Leaving heater 538 is heated gas stream 540 which is diverted into one of the two adsorption columns through the control of switching valves 542 and 544. When passed through either adsorption column 512 or second adsorption column 518, heated gas stream 540 removes the isobutanol and water from the solid adsorbent. Leaving either adsorption column is isobutanol/water rich gas stream 546. Isobutanol/water rich gas stream 546 then enters gas chiller 548 which causes the vaporous isobutanol and water in isobutanol/water rich gas stream 546 to condense into a liquid phase that is separate from the other noncondensable species in the stream. Leaving gas chiller 548 is a biphasic gas stream 550 which is fed into decanter 534. In decanter 534 the condensed isobutanol/water phase is separated from the gas stream. Leaving decanter 534 is an aqueous isobutanol stream

12

552 which is then fed to a distillation apparatus that is capable of separating aqueous isobutanol from ethanol, or used directly as a feed to a reaction vessel (not shown) in which the aqueous isobutanol is catalytically converted to a reaction product that comprises at least one isooctene. Also leaving decanter 534 is cooled gas stream 532.

Referring now to FIG. 6, there is shown a block diagram for refining apparatus 600, suitable for producing an aqueous isobutanol stream, when the fermentation broth comprises isobutanol and water, and may additionally comprise ethanol. Fermentor 602 contains a fermentation broth comprising isobutanol and water and a gas phase comprising CO₂ and to a lesser extent some vaporous isobutanol and water. Both phases may additionally comprise ethanol. An isobutanol-containing fermentation broth stream 604 leaving fermentor 602 is introduced into cell separator 606. Isobutanol-containing stream 604 may contain some non-condensable gas species, such as carbon dioxide. Cell separator 606 can be comprised of centrifuges or membrane units to accomplish the separation of cells from the fermentation broth. Leaving cell separator 606 is concentrated cell stream 608 that is recycled back to fermentor 602. Also leaving cell separator 606 is clarified fermentation broth stream 610. Clarified fermentation broth stream 610 can then be introduced into optional heater 612 where it is optionally raised to a temperature of 40 to 80° C. Leaving optional heater 612 is optionally heated clarified broth stream 614. Optionally heated clarified broth stream 614 is then introduced to the liquid side of first pervaporation module 616. First pervaporation module 616 contains a liquid side that is separated from a low pressure or gas phase side by a membrane (not shown). The membrane serves to keep the phases separated and also exhibits a certain affinity for isobutanol. In the process of pervaporation any number of pervaporation modules can be used to effect the separation. The number is determined by the concentration of species to be removed and the size of the streams to be processed. Diagrammatically, two pervaporation units are shown in FIG. 6, although any number of units can be used. In first pervaporation module 616 isobutanol is selectively removed from the liquid phase through a concentration gradient caused when a vacuum is applied to the low pressure side of the membrane. Optionally a sweep gas can be applied to the non-liquid side of the membrane to accomplish a similar purpose. The first depleted isobutanol stream 618 exiting first pervaporation module 616 then enters second pervaporation module 620. Second isobutanol depleted stream 622 exiting second pervaporation module 620 is then recycled back to fermentor 602. The low pressure streams 619, 621 exiting first and second pervaporation modules 616 and 620, respectively, are combined to form low pressure isobutanol/water stream 624. Low pressure isobutanol stream/water 624 is then fed into cooler 626 where the isobutanol and water in low pressure isobutanol/water stream 624 is caused to condense. Leaving cooler 626 is condensed low pressure isobutanol/water stream 628. Condensed low pressure isobutanol/water stream 628 is then fed to receiver vessel 630 where the condensed isobutanol/water stream collects and is withdrawn as stream 632. Vacuum pump 636 is connected to the receiving vessel 630 by a connector 634, thereby supplying vacuum to apparatus 600. Non-condensable gas stream 634 exits decanter 630 and is fed to vacuum pump 636. Aqueous isobutanol stream 632 is then fed to a distillation apparatus that is capable of separating aqueous isobutanol from ethanol, or is used directly as a feed to a reaction vessel (not shown) in which the aqueous isobutanol is catalytically converted to a reaction product that comprises at least one isooctene.

Referring now to FIG. 7, there is shown a block diagram for refining apparatus 700, suitable for producing an aqueous isobutanol stream, when the fermentation broth comprises isobutanol, ethanol, and water. A stream 702 of fermentation broth is introduced into a feed preheater 704 to raise the broth temperature to produce a heated feed stream 706 which is introduced into a beer column 708. The beer column 708 needs to have a sufficient number of theoretical stages to cause separation of a ternary azeotrope of isobutanol, ethanol, and water to be removed as an overhead product stream 710 and a hot water bottoms stream 712. Hot water bottoms stream 712, is used to supply heat to feed preheater 704 and leaves as lower temperature bottoms stream 714. Reboiler 716 is used to supply heat to beer column 708. Overhead stream 710 is a ternary azeotrope of isobutanol, ethanol and water and is fed to ethanol column 718. Ethanol column 718 contains a sufficient number of theoretical stages to effect the separation of an ethanol water azeotrope as overhead stream 720 and biphasic bottoms stream 721 comprising isobutanol, ethanol and water. Biphasic bottoms stream 721 is then fed to cooler 722 where the temperature is lowered to ensure complete phase separation. Leaving cooler 722 is cooled bottoms stream 723 which is then introduced into decanter 724 where an isobutanol rich phase 726 is allowed to phase separate from a water rich phase 728. Both phases still contain some amount of ethanol. A water rich phase stream 730 comprising a small amount of ethanol and isobutanol is returned to beer column 708. An isobutanol rich stream 732 comprising a small amount of water and ethanol is fed to isobutanol column 734. Isobutanol column 734 is equipped with reboiler 736 necessary to supply heat to the column. Isobutanol column 734 is equipped with a sufficient amount of theoretical stages to produce a isobutanol/water bottoms stream 738 and an ethanol/water azeotropic stream 740 that is returned to ethanol column 718. Isobutanol/water bottoms stream 738 (i.e., aqueous isobutanol stream) can then be used as a feed to a reaction vessel (not shown) in which the aqueous isobutanol is catalytically converted to a reaction product that comprises at least one isooctene.

The at least one recovered isooctene can be further converted to isooctanes, isooctanols or isooctyl alkyl ethers, which are useful fuel additives. The terms isooctanes and isooctanols are meant to denote eight-carbon compounds having at least one secondary or tertiary carbon. The term isooctyl alkyl ether is meant to denote a compound, the isooctyl moiety of which contains eight carbons, at least one carbon of which is a secondary or tertiary carbon.

In one embodiment of the invention, the at least one isooctene is contacted with at least one hydrogenation catalyst in the presence of hydrogen to produce a reaction product comprising at least one isooctane. Suitable solvents, catalysts, apparatus, and procedures for hydrogenation in general can be found in Augustine, R. L. (Heterogeneous Catalysis for the Synthetic Chemist, Marcel Decker, New York, 1996, Section 3); the hydrogenation can be performed as exemplified in U.S. Patent Application No. 2005/0054861, paragraphs 17-36). In general, the reaction is performed at a temperature of from about 50 degrees Centigrade to about 300 degrees Centigrade, and at a pressure of from about 0.1 MPa to about 20 MPa. The principal component of the hydrogenation catalyst may be selected from metals from the group consisting of palladium, ruthenium, rhodium, iridium, platinum, nickel, cobalt, copper, iron, osmium; compounds thereof; and combinations thereof. The catalyst may be supported or unsupported. The at least one isooctane can be separated from the hydrogenation catalyst by any suitable method, including decantation. The at least one isooctane can

then be recovered (for example, if the reaction does not go to completion or if a homogeneous catalyst is used) from the reaction product by distillation (see Seader, J. D., supra) to obtain a recovered isooctane, and added to a transportation fuel. Alternatively, the reaction product itself can be added to a transportation fuel. If present, unreacted isooctenes can be used in subsequent reactions to produce isooctanes.

In another embodiment, the at least one isooctene is contacted with water in the presence of at least one acidic catalyst to produce a reaction product comprising at least one isooctanol. The hydration of olefins is well known, and a method to carry out the hydration using a zeolite catalyst is described in U.S. Pat. No. 5,288,924 (Column 3, line 48 to Column 7, line 66), wherein a temperature of from about 60 degrees Centigrade to about 450 degrees Centigrade and a pressure of from about 700 kPa to about 24,500 kPa are used. The water to olefin ratio is from about 0.05 to about 30. Where a solid acid catalyst is used, such as a zeolite, the at least one isooctanol can be separated from the at least one acid catalyst by any suitable method, including decantation. The at least one isooctanol can then be recovered from the reaction product by distillation (see Seader, J. D., supra) to obtain a recovered isooctanol, and added to a transportation fuel. Alternatively, the reaction product itself can be added to a transportation fuel. Unreacted isooctenes, if present, can be used in subsequent reactions to produce isooctanols.

In still another embodiment, the at least one isooctene is contacted with at least one acid catalyst in the presence of at least one straight-chain or branched C₁ to C₅ alcohol to produce a reaction product comprising at least one isooctyl alkyl ether. One skilled in the art will recognize that C₁ and C₂ alcohols cannot be branched. The etherification reaction is described by Stüwe, A., et al (Synthesis of MTBE and TAME and related reactions, Section 3.11, in Handbook of Heterogeneous Catalysis, Volume 4, (Ertl, G., Knözinger, H., and Weitkamp, J. (eds), 1997, VCH Verlagsgesellschaft mbH, Weinheim, Germany)) for the production of methyl-t-butyl ether. The etherification reaction is generally carried out at temperature of from about 50 degrees Centigrade to about 200 degrees Centigrade at a pressure of from about 0.1 to about 20.7 MPa. Suitable acid catalysts include, but are not limited to, acidic ion exchange resins. Where a solid acid catalyst is used, such as an ion-exchange resin, the at least one isooctyl alkyl ether can be separated from the at least one acid catalyst by any suitable method, including decantation. The at least one isooctyl alkyl ether can then optionally be recovered from the reaction product by distillation (see Seader, J. D., supra) to obtain a recovered isooctyl alkyl ether, and added to a transportation fuel. If present, unreacted isooctenes can be used in subsequent reactions to produce isooctyl alkyl ethers.

According to embodiments described above, isooctenes produced by the reaction of aqueous isobutanol with at least one acid catalyst are first recovered from the reaction product prior to being converted to compounds useful in transportation fuels. However, as described in the following embodiments, the reaction product comprising isooctenes can also be used in subsequent reactions without first recovering said isooctenes.

Thus, one alternative embodiment of the invention is a process for making at least one isooctane comprising:

(a) contacting a reactant comprising isobutanol and at least about 5% water (by weight relative to the weight of the water plus isobutanol) with at least one acid catalyst at a temperature of about 50 degrees C. to about 450 degrees C. and a pressure from about 0.1 MPa to about 20.7 MPa to produce a first reaction product comprising at least one isooctene;

15

(b) contacting said first reaction product with hydrogen in the presence of at least one hydrogenation catalyst to produce a second reaction product comprising at least one isooctane; and

(c) recovering the at least one isooctane from the second reaction product to produce a recovered isooctane.

The at least one recovered isooctane can then be added to a transportation fuel.

Another embodiment of the invention is a process for making at least one isooctanol comprising:

16

The examples below were performed according to this procedure under the conditions indicated for each example.

EXAMPLES 1-5

Reaction of Isobutanol (Iso-BuOH) with an Acid Catalyst to Produce Isooctenes

The feedstock was 85 wt. % isobutanol/15 wt. % water. Abbreviations: Press is pressure; Conv is conversion; Sel is selectivity.

Example Number	Catalyst	Catalyst Loading (mg)	Time (hr)	Temp (C.)	N ₂ Press (MPa)	iso-BuOH % Conv	Isooctenes % Sel
1	Amberlyst® 15	107	2	200	6.6	53.5	54.1
2	13% Nafion®/SiO ₂	119	2	200	6.6	4.0	2.2
3	CBV-3020E	102	2	200	6.6	49.8	45.6
4	H-Mordenite	103	2	200	6.6	47.0	42.7
5	Sulfuric Acid	54	2	200	6.6	96.3	61.3

(a) contacting a reactant comprising isobutanol and at least about 5% water (by weight relative to the weight of the water plus isobutanol) with at least one acid catalyst at a temperature of about 50 degrees C. to about 450 degrees C. and a pressure from about 0.1 MPa to about 20.7 MPa to produce a first reaction product comprising at least one isooctene;

(c) contacting said first reaction product with water and at least one acid catalyst to produce a second reaction product comprising at least one isooctanol; and

(d) optionally recovering the at least one isooctanol from the second reaction product to obtain at least one recovered isooctanol.

The third reaction product or the at least one recovered isooctane can then be added to a transportation fuel.

GENERAL METHODS AND MATERIALS

In the following examples, "C" is degrees Centigrade, "mg" is milligram; "ml" is milliliter; "MPa" is mega Pascal; "wt. %" is weight percent; "GC/MS" is gas chromatography/mass spectrometry.

Amberlyst® (manufactured by Rohm and Haas, Philadelphia, Pa.), isobutanol and H₂SO₄ were obtained from Alfa Aesar (Ward Hill, Mass.); CBV-3020E was obtained from PQ Corporation (Berwyn, Pa.); 13% Nafion®/SiO₂ can be obtained from Engelhard; and H-Mordenite can be obtained from Zeolyst Intl. (Valley Forge, Pa.).

General Procedure for the Conversion of Isobutanol to Isooctenes

A mixture of isobutanol, water, and catalyst was contained in a 2 ml vial equipped with a magnetic stir bar. The vial was sealed with a serum cap perforated with a needle to facilitate gas exchange. The vial was placed in a block heater enclosed in a pressure vessel. The vessel was purged with nitrogen and the pressure was set at 6.9 MPa. The block was brought to the indicated temperature and controlled at that temperature for the time indicated. After cooling and venting, the contents of the vial were analyzed by GC/MS using a capillary column (either (a) CP-Wax 58 [Varian; Palo Alto, Calif.], 25 m×0.25 mm, 45 C/6 min, 10 C/min up to 200 C, 200 C/10 min, or (b) DB-1701 [J&W (available through Agilent; Palo Alto, Calif.)], 30 m×0.25 mm, 50 C/10 min, 10 C/min up to 250 C, 250 C/2 min).

As those skilled in the art of catalysis know, when working with any catalyst, the reaction conditions need to be optimized. Examples 1 to 5 show that the indicated catalysts were capable under the indicated conditions of producing the product isooctenes. Some of the catalysts shown in Examples 1 to 5 were ineffective when utilized at suboptimal conditions (e.g., lower temperature) (data not shown).

The invention claimed is:

1. A process for production of gasoline, diesel fuel, jet fuel, or transportation fuel additive comprising:

producing isobutanol from a feedstock derived from a renewable source by a genetically modified microorganism via a biosynthetic pathway comprising substrate to product conversions that include:

pyruvate to acetolactate;
acetolactate to 2,3-dihydroxyisovalerate;
2,3-dihydroxyisovalerate to α -ketoisovalerate;
 α -ketoisovalerate to isobutyraldehyde; and
isobutyraldehyde to the isobutanol; and

reacting the isobutanol to produce an intermediate for the production of gasoline, diesel fuel, jet fuel, or transportation fuel additive.

2. The process of claim 1, wherein the genetically modified microorganism is tolerant to isobutanol at levels greater than 1% weight per volume.

3. The process of claim 1, further comprising refining the isobutanol prior to the reacting, wherein the isobutanol that results from the distillation is substantially free of one or more of ethanol or acetone.

4. The process of claim 3, wherein the refining yields an aqueous stream that comprises at least about 5% water by weight of the water and isobutanol.

5. The process of claim 1, wherein reacting comprises contacting the isobutanol with at least one acid catalyst.

6. The process of claim 5, wherein the intermediate comprises isooctene, dibutyl ether, or butene.

7. The process of claim 6, further comprising recovering the isooctene and converting the isooctene to isooctane, isooctanol, or isooctyl alkyl ether.

8. The process of claim 7, wherein converting comprises contacting the isooctene with a hydrogenation catalyst in the presence of hydrogen.

17

9. The process of claim 7, further comprising:
recovering the isooctane, isooctanol, or isooctyl alkyl
ether; and
adding the isooctane, isooctanol, or isooctyl alkyl ether
that is recovered to a transportation fuel.

10. The process of claim 6, further comprising contacting
the isooctene with an acid catalyst in the presence of at least
one straight-chain or branched C1 to C5 alcohol.

11. A process for production of gasoline, diesel fuel, jet
fuel, or transportation fuel additive comprising:

obtaining isobutanol that is essentially free of ethanol and
is produced by a genetically modified microorganism
via a biosynthetic pathway that implements a fermenta-
tion broth, the biosynthetic pathway comprising:

pyruvate to acetolactate;
acetolactate to 2,3-dihydroxyisovalerate;
2,3-dihydroxyisovalerate to α -ketoisovalerate;
 α -ketoisovalerate to isobutyraldehyde; and
isobutyraldehyde to the isobutanol; and

contacting the isobutanol with an acid catalyst to produce
an intermediate for the production of gasoline, diesel
fuel, jet fuel, or transportation fuel additive.

18

12. The process of claim 11, wherein contacting comprises
contacting the isobutanol with the acid catalyst in an aqueous
solution where water is at least about five percent (5%) by
weight.

13. The process of claim 11, wherein the intermediate
comprises at least one of isooctene, dibutyl ether, or butene.

14. The process of claim 13, further comprising converting
the intermediate to isooctane by contacting the intermediate
with a hydrogenation catalyst in the presence of hydrogen.

15. The process of claim 13, further comprising contacting
the intermediate with water in the presence of at least one
acidic catalyst and least one straight-chain or branched C1 to
C5 alcohol to produce isooctyl alkyl ether.

16. The process of claim 11, wherein the genetically modi-
fied microorganism is tolerant to isobutanol at levels greater
than 1% weight per volume.

17. The process of claim 11, wherein the fermentation
broth contains at least about fifty percent (50%) isobutanol by
weight to water in the fermentation broth.

* * * * *